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Boron accumulation by maize grown in acidic soil amended with coal combustion products

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Abstract

Coal combustion products (CCPs) have potential for use as soil amendments on acidic soils. One concern for plants grown on acidic soils amended with CCPs is boron (B) toxicity, since many CCPs contain considerable B. Maize (*Zea mays* L.) was grown (greenhouse) on acidic soil [Umbric Dystrochept, pH 3.9 (1 soil:1 10 *mM* $CaCl_2$)] amended with 15 CCPs [two fly ashes (FAs), three fluidized bed combustion products (FBCs), one calcium (Ca) oxide (CaO) material, six high Ca sulfite ($CaSO_3$) flue gas desulfurization products (FGDs), and three high Ca sulfate ($CaSO_4$) FGDs] at different levels to determine accumulation of B in shoots. Plants were also grown in soil amended with Ca carbonate ($CaCO_3$, lime) and chemical grade $CaSO_4$ and $CaSO_3$ as controls. Among the CCPs tested, FAs contained the highest B levels. Shoot B concentrations were as high as 500 mg kg^{-1} without reductions in dry matter (DM) for plants grown on soil amended with one FA. Plants grown with one FBC had sufficient B to suspect potential B toxicity, and plant DM was greatly reduced or died when grown with $> 0.5\%$ of this material. Relatively high shoot B concentrations were noted in plants grown with the highest levels of high $CaSO_3$ FGDs. High shoot B concentrations ($\sim$300 mg kg^{-1}) were noted for plants grown with $> 5\%$ levels of one high $CaSO_4$ FGD, and DM declined after reaching these levels. Plants grown on soil amended with CaO had low shoot B. Some of the CCPs used in this study contained sufficient B to potentially induce B toxicity in plants grown on the acidic soil amended with the various CCPs. Maize growth was generally enhanced when grown on soil amended with the CCPs at appropriate levels. Published by Elsevier Science Ltd.

Keywords: Plant dry matter; Shoot boron concentrations; Soil pH and electrical conductivity

1. Introduction

Large amounts of coal combustion products (CCPs) are produced (92.4 million metric tons in 1996 [1]) when coal is burned to generate electricity. Beneficial uses of CCPs are desired when these materials are discarded. Only $\sim 25\%$ of the CCPs produced were being used beneficially in 1996 [1]. One beneficial use of CCPs could be as a soil amendment (source of mineral nutrients, substitute for limestone, and conditioner of physical soil properties) on agricultural/pasture/forest land, especially on acidic soils [2, 3]. One concern when using certain CCPs on soil is the potential toxicity of boron (B) to plants.

Various types of CCPs are produced, which have generally been categorized as fly ashes (FAs), bottom ashes, boiler slags, and flue gas desulfurization products (FGDs) [1]. Each CCP group has different physico-chemical properties depending on the source of burned materials and burning operations at power plants. In addition, CCPs are often mixed together, especially to stabilize wet high calcium (Ca) sulfite ($CaSO_3$) FGDs. The stabilization materials usually added are FAs, fluidized bed combustion products (FBCs), and/or Ca oxide (CaO) materials. The amount of B in CCPs can vary considerably.

Boron is required for plant growth, but is generally toxic at levels slightly above those required for normal growth [4]. Thus, the margin between B sufficiency and toxicity to plants is narrow. In addition, some plants are more sensitive to B toxicity or deficiency than others. For example, legumes and dicotyledonous plants generally require higher B than grasses and monocotyledonous plants. Many fruits (e.g., grapes, apples, pears) also have high B requirements. Boron is readily adsorbed to soil particles, and B availability generally decreases as soil pH increases [4]. Thus, liming can reduce plant uptake of B even when B levels applied to soils are relatively high. Boron is also highly soluble in water and may readily leach.

Boron in some CCPs, especially FAs and FBCs, may be sufficiently high to potentially induce B toxicity in some

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Table 1
The pH, electrical conductivity (EC) and B concentrations in CCPs used to amend acidic soil

Type of CCP	CCP No.[a]	pH[b]	EC[b] (dS m^{-1})	B in CCP (mg kg^{-1})
FA	BP-#12	12.89	3.54	431
	BP-#18	12.68	1.82	358
FBC	BP-#15	13.59	7.77	8
	BP-#21	13.17	5.56	75
	BP-#26	12.80	8.45	171
CaO	BP-#10	13.67	6.72	<1
FGD (high $CaSO_3$)	BP-#1	9.76	3.38	46
	BP-#2	10.76	4.65	98
	BP-#4	9.50	4.04	53
	BP-#5	10.43	2.77	171
	BP-#6	9.43	3.54	145
	BP-#8	11.27	2.94	175
FGD (high $CaSO_4$)	BP-#16	9.31	1.73	<1
	BP-#22	8.96	1.92	<1
	BP-#27	9.65	3.29	99

[a] Numbers for products are the same as described in Clark et al. [14]
[b] pH and EC = 1 soil:2 water

Table 2
Ranges of soil pH_{Ca} and electrical conductivity (EC) of acidic soil amended with $CaCO_3$, $CaSO_4$, $CaSO_3$, and CCPs (see Tables 3–6 for levels of control materials and CCP added to soil)

Type of CCP	CCP No.[a]	Soil pH_{Ca} range[b]	Soil EC range[c] (dS m^{-1})
Unamended soil		3.82–4.03	0.09–0.17
Controls	$CaCO_3$	3.94–6.03	0.11–0.20
	$CaSO_4$	3.99–6.54	0.11–1.46
	$CaSO_3$	3.94–4.49	0.11–1.70
FA	BP-#12	3.91–4.82	0.17–0.94
	BP-#18	4.03–7.60	0.12–6.47
FBC	BP-#15	4.00–8.19	0.09–1.83
	BP-#21	4.03–8.25	0.12–2.50
	BP-#26	3.82–10.40	0.10–1.96
CaO	BP-#10	3.91–9.82	0.17–0.75
FGD (high $CaSO_3$)	BP-#1	3.94–4.94	0.11–1.46
	BP-#2	3.94–6.46	0.11–1.98
	BP-#4	3.91–5.62	0.17–3.00
	BP-#5	3.91–5.93	0.17–2.31
	BP-#6	4.00–4.64	0.09–1.74
	BP-#8	4.00–5.38	0.09–2.08
FGD (high $CaSO_4$)	BP-#16	4.00–5.52	0.11–1.68
	BP-#22	4.00–6.54	0.11–1.20
	BP-#27	3.82–8.30	0.10–3.20

[a] Numbers for products are the same as described in Clark et al. [14]
[b] pH_{Ca} = 1 soil:1 10 *mM* $CaCl_2$
[c] EC = 1 soil:1 water

Table 3
Whole plant dry matter (DM) and shoot B concentrations [standard error of means in ( )] for maize grown in acidic soil amended with chemical grade $CaCO_3$, $CaSO_4$, and $CaSO_3$

Material	Level in soil mix (%)	Plant DM (mg plant^{-1})	Shoot B (mg kg^{-1})
$CaCO_3$ (lime)[a]	0	318	21.7(4.0)
	0.05	448	20.1(5.2)
	0.10	496	16.5(3.1)
	0.25	566	12.7(3.6)
	0.5	617	8.1(2.1)
	1.0	576	4.8(1.8)
$CaSO_4$	0	466(31)	15.2(2.7)
	0.25	285(41)	17.7(2.4)
	0.5	189(14)	20.8(2.4)
	1	216(31)	18.3(2.5)
	2	313(15)	16.4(3.0)
	4	374(43)	16.4(3.2)
	0	368(19)	21.7(4.0)
	5	392(20)	15.2(2.7)
	10	516(63)	16.8(6.1)
	25	579(27)	13.6(0.4)
	50	409(51)	15.8(2.6)
	75	360(13)	11.4(0.8)
$CaSO_3$	0	466(31)	21.7(4.0)
	0.25	307(40)	20.8(4.4)
	0.5	231(41)	24.3(1.2)
	1	222(27)	22.3(6.3)
	2	136(24)	20.0(0.6)
	4	61(14)	10.9(1.5)

[a] The DM means relative to $CaCO_3$ are for at least three and as high as six experiments, except for the 1.0% level which is the mean for one experiment. Thus, no standard error of means for these DM values have been provided

plants grown with these residues unless B is removed or leached [5]. Leaching to reduce levels of B (and some other mineral elements) from CCPs before applying to soil has been recommended [6, 7]. The level of B must be considered when CCPs are applied to soils for growth of certain plants [8, 9]. Levels of B were relatively high in the soil incorporation zone where mixtures of FBC and FA had been added simultaneously to reduce soil acidity [10].

Toxicity concentrations of B in plants vary, but B above $\sim$ 50–100 mg kg^{-1} has been considered high for many plants [11, 12]. For maize (*Zea mays* L.), B has been considered to be high at $>$ 25 mg kg^{-1} in shoots of young plants [11] and at $>$ 100 mg kg^{-1} in leaves of plants near tasselling or ear formation [12]. For maize grown to maturity where nutrients were continuously supplied (nutrient solutions), ear leaves had $\sim$ 50 mg kg^{-1} B near silking, and increased to 100–130 mg kg^{-1} at maturity [13]. In addition, B concentrations in these maize plants increased in leaves at higher positions on the plant, and the flag (uppermost) leaf had $\sim$ 200 mg kg^{-1} at maturity with no B toxicity symptoms. Concentrations of B for severe toxicity have been reported at 270–570 mg kg^{-1} for grasses and 960 mg kg^{-1} for the needles of conifer trees [4].

Since CCPs have potential use as soil amendments, especially on acidic soils, and B toxicity has been identified as a potential problem for plants grown on soils amended with CCPs, experiments were conducted to determine B concentrations in shoots of young maize grown in acidic soil amended with varied levels of several CCPs.

2. Experimental

An acidic Porters (coarse-loamy, mixed, mesic, Umbric Dystrochrept) soil from eastern Tennessee (farmland near the edge of woods) was used in the experiments. Initial soil pH was 4.22 (1 soil:1 water) and 3.88 (1 soil:1 10 *mM* $CaCl_2$). The CCPs used in the experiments were two FAs (BP-#12 and BP-#18), three FBCs (BP-#15, BP-#21, and BP-#26), one CaO material (BP-#10), six high $CaSO_3$ FGDs (BP-#1, BP-#2, BP-#4, BP-#5, BP-#6, and BP-#8), and three high $CaSO_4$ FGDs (BP-#16, BP-#22, and BP-#27). The pH and electrical conductivity (EC, soluble salts) and B concentrations in the CCPs are listed in Table 1. Descriptions and many physico-chemical properties of the CCPs have been provided elsewhere [14]. Chemical grade $CaSO_3$ and Ca sulfate ($CaSO_4$) were included as controls in some experiments. Unamended soil and varied levels of Ca carbonate ($CaCO_3$, lime) treatments were included in each experiment.

Table 4
Whole plant dry matter (DM) and shoot B concentration [standard error of means in ( )] of maize grown on acidic soil amended with FAs, CaO, and FBCs

Trait	Level in soil mix (%)	FAs[a]		CaO[a]	FBCs[a]		
		BP-#12	BP-#18	BP-#10	BP-#15	BP-#21	BP-#26
Plant DM (mg per plant)	0	449(65)	471(46)	449(65)	606(32)	576(71)	251(6)
	0.5		901(38)		1156(88)	1053(42)	319(22)
	1	695(56)	940(62)	794(39)	1122(101)	1263(82)	71(8)
	2	741(28)	989(60)	638(43)	822(52)	1021(29)	
	2.5						32(9)
	3	861(38)	993(44)	493(80)	602(73)	1105(37)	
	5	676(32)	985(40)	418(88)	459(47)	817(81)	28(6)
	10	536(59)	1095(77)	55(4)		636(45)	33(3)
	20					341(12)	49(8)
	25		979(36)				
Shoot B (mg kg^{-1})	0	38(8)	17(1)	37.8(8.9)	27.6(5.4)	18.2(2.0)	10.8(1.7)
	0.5		62(12)		14.4(3.3)	28.0(2.6)	71.7(1.7)
	1	169(9)	163(12)	14.9(2.1)	16.3(4.7)	23.8(2.3)	173[b]
	2	314(20)	–	13.6(7.7)	38.9(5.3)	29.0(4.2)	
	2.5						ND[c]
	3	431(15)	224(14)	20.9(4.5)	47.2(9.2)	28.6(3.2)	
	5	781(76)	290(9)	20.0(4.7)	25.0(2.3)	24.1(1.7)	ND
	10	1207(136)	181(10)	21.4(7.8)		17.0(1.4)	ND
	20					24.2(0.7)	ND
	25		227(8)				

[a] Numbers for products are the same as described in Clark et al. [14]
[b] Sufficient tissue for analysis of only one sample
[c] ND = insufficient tissue for analysis

Each CCP or control material and fertilizer (100 mg nitrogen as ammonium nitrate and 400 mg phosphorus as potassium dihydrogen phosphate per kg soil) were thoroughly mixed with soil. Levels of each CCP and control material added to soil are listed in Tables 3–6. Deionized water was added to soil mixes to provide -0.033 MPa tension (near water holding capacity of soil) and equilibrated 7 days before being placed in pots (1.0 kg soil mix in each pot) for plant growth. Because of the large number of CCPs and control materials and levels used, several experiments were conducted over time. Each experiment had completely randomized blocks with four replications.

Seeds of the maize hybrid PA329 × PA353P were surface sterilized with 0.1-strength sodium hypochlorite (household

Table 5
Whole plant dry matter (DM) and shoot B concentration [standard error of means in ( )] of maize grown on acidic soil amended with high $CaSO_3$ FGDs

Trait	Level in soil mix (%)	High $CaSO_3$ FGDs[a]					
		BP-#1	BP-#2	BP-#4	BP-#5	BP-#6	BP-#8
Plant DM (mg per plant)	0	466(31)	466(31)	449(65)	449(65)	606(32)	606(32)
	0.5	524(52)	662(64)			807(32)	942(71)
	1	552(21)	580(20)	472(27)	543(34)	692(39)	948(151)
	2	366(14)	172(27)	213(29)	631(15)	472(64)	1130(61)
	3	187(14)	86(17)	155(43)	515(64)	275(36)	825(32)
	5	124(22)	95(13)	126(11)	365(59)	238(45)	511(54)
	10			47(2)	69(7)		
Shoot B (mg kg^{-1})	0	15.2(2.7)	15.2(2.7)	37.8(8.9)	38(8)	27.6(5.4)	27.6(5.4)
	0.5	15.7(1.1)	28.3(3.6)			40.9(6.4)	49.0(5.1)
	1	32.1(0.5)	46.5(4.1)	32.3(6.3)	57(3)	63.9(5.3)	53.3(12.1)
	2	73.9(8.2)	108.3(9.3)	66.8(9.7)	120(12)	85.7(5.0)	151.3(18.0)
	3	104.6(4.7)	131.3(9.4)	84.2(8.0)	162(26)	161.7(9.5)	207.4(23.5)
	5	167.8(10.7)	136.1(7.2)	118.9(6.9)	257(10)	193.0(57.9)	255.3(34.9)
	10			122.9(7.0)	479(31)		

[a] Numbers for products are the same as described in Clark et al. [14]

Table 6
Whole plant dry matter (DM) and shoot B concentration [standard error of means in ( )] of maize grown on acidic soil amended with high $CaSO_4$ FGDs

Trait	Level in soil mix (%)	High $CaSO_4$ FGDs[a]		
		BP-#16	BP-#22	BP-#27
Plant DM (mg per plant)	0	188(17)	190(15)	251(6)
	1			677(24)
	2.5			653(20)
	5	181(15)	275(8)	528(34)
	10	185(17)	369(21)	446(17)
	25	247(40)	467(29)	263(28)
	50	434(29)	402(36)	114(11)
	75	348(64)	364(31)	
Shoot B (mg kg^{-1})	0	22.4(3.5)	17.2(1.6)	11(1)
	1			77(3)
	2.5			170(11)
	5	19.4(1.9)	17.2(2.1)	350(105)
	10	24.4(1.4)	14.8(2.5)	358(111)
	25	36.0(4.2)	17.2(3.3)	348(43)
	50	65.7(8.3)	24.0(1.5)	231(27)
	75	106.4(6.1)	65.2(3.0)	

[a] Numbers for products are the same as described in Clark et al. [14]

bleach) for 5 min, rinsed thoroughly with deionized water, and germinated between wrapped germination papers moistened with deionized water containing dilute $CaSO_4$ to assure good root development. Three 3 day-old seedlings were transplanted to each pot. Deionized water was added manually every other day initially and daily after plants became established to avoid splashing on stalks and leaves, to provide sufficient moisture for plant growth, and to prevent leaching from pots. Experiments were conducted in a greenhouse (25 ± 3°C) using natural and artificial light (to extend short days to 14 h of light and provide extra light during cloudy days when artificial light was needed). High-pressure sodium lamps provided artificial light at 400–500 μmol m^{-2} s^{-1} at plant height. Plants were grown in treated soil for 21 days.

Plants were harvested by severing shoots ~ 1 cm above the soil surface. Shoots were dried, weighed, and ground to pass a 0.5 mm screen in preparation for B analysis. Roots were removed from soil and placed on a screen. Soil samples were collected for determination of pH and EC. Roots were thoroughly washed free of soil, blotted dry, and weighed.

Each sample of ground shoot material was weighed (50–100 mg) into separate teflon containers, digestion solution (1.7 mL 15.8 *M* HNO_3 + 0.2 mL 11.4 *M* HCl + 0.1 mL 28.9 *M* HF) was added, and containers were placed in microwave digestion bombs (Parr Instrument, Moline, IL[1]). These samples were microwaved for 4 min at 70% power, then for 2 min at full power (635 W delivered), allowed to cool in the microwave oven (~ 5 min), and removed to cool at ambient temperature. Digested solutions were brought to a final volume of 10.0 mL with distilled deionized water. Solutions were filtered and stored in plastic containers at − 10°C until analyzed for B by inductively coupled plasma spectroscopy (Model 3580, Applied Research Laboratories, Dearborn, MI).

3. Results and discussion

Some CCPs and the control materials ($CaCO_3$, $CaSO_3$, $CaSO_4$) used in these studies increased soil pH and EC when added to the acidic soil. Some CCPs increased soil pH and EC more than others (Table 2). Even relatively low levels of some CCPs and the $CaCO_3$ raised soil pH to relatively high values (see Tables 3–6 for levels of the CCPs and $CaCO_3$ added). Changes in soil pH and EC from CCP amendment (Table 2) were as might be expected from the original CCP pH and EC values (Table 1).

A $CaCO_3$ level of 1.0% (22 ton ha^{-1}) increased soil pH from 3.94 to 6.03, which approached a level that might induce ‘‘overliming stress’’ effects on plants [15–17]. Other experiments have been conducted where > 1.0% $CaCO_3$ had been added to acidic soil and soil pH increased to > 7.0, and plant DM decreased below a maximum obtained at lower levels of $CaCO_3$ [18]. Similar results have been associated with reduced availability of nutrients, especially Mg [17]. Chemical grade $CaSO_4$ and $CaSO_3$ had relatively minor effects on raising soil pH at low levels (<

[1] Mention of company or commercial products does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

5% in soil mix), and $CaSO_4$ at 75% in soil mixes increased soil pH to only 6.5 (Table 2).

Only the FBCs and CaO at the highest levels used in these studies raised soil pH (Table 2) to the extent that plants would likely be detrimentally affected from overliming or high soil pH. Since B availability in soil decreases with increased soil pH [4], the higher pH of soils amended with many of the CCPs compared to no added CCP would likely decrease the potential of maize plants to accumulate high B. Lower shoot B concentrations were noted for maize grown with higher compared to lower levels of $CaCO_3$, and at the highest levels of $CaSO_4$ and $CaSO_3$ (Table 3). Similar results were noted for maize grown on acidic soil amended with varied levels of $CaCO_3$ and B in other studies [18].

Salts added to soil commonly increase soil B, since B is a common element in many salt materials. As such, addition of CCPs containing salts to soil might not only add excess B, but also other elements to detrimentally affect plant growth. Plant species differ in tolerance to salt level, and maize is considered to be moderately salt sensitive [19]. The EC of soils for threshold salt toxicity to moderately sensitive plants ranges from ~ 1.5 to 3.0 dS m^{-1} [19]. The highest levels of chemical grade $CaCO_3$, $CaSO_4$, and $CaSO_3$ did not increase soil EC sufficiently (Table 2) to be detrimental to maize growth (Table 3). The CCPs which increased soil EC sufficiently (Table 2) to potentially decrease plant DM for moderately sensitive plants would have been BP-#18 at 25% (Table 4), BP-#4 at 10% (Table 5), and BP-#27 at 50% in soil (Table 6). Additional information about soil pH and EC at the various levels of CCPs and control substances added to acidic soil is reported elsewhere [14, 20].

Plants grown in the acidic soil amended with varied levels of control materials ($CaCO_3$, $CaSO_4$, and $CaSO_3$) had relatively low concentrations of B in shoots (Table 3), which were considered normal for healthy plants [11, 12]. However, plants grown in the acidic soil amended with several of the CCPs had sufficient B in shoots that B toxicity was a concern (Tables 4–6). Since reported B concentrations in young maize shoots considered to be high have been > 25 mg kg^{-1} [11] and potentially toxic at concentrations > 100 mg kg^{-1} [12], shoot B concentrations of 50–100 mg kg^{-1} dry tissue might be of concern. Shoot B concentrations needed to be 150–200 mg kg^{-1} for DM of 24 day-old maize to decrease from a maximum when grown on acidic soil amended with various levels of B and $CaCO_3$ [18]. Shoots accumulating B at potential toxic concentrations (> 200 mg kg^{-1}) were plants grown on acidic soil amended with BP-#12 and BP-#18 (FAs) (Table 4), BP-#5 and BP-#8 (stabilized high $CaSO_3$ FGDs) (Table 5), and BP-#27 (high $CaSO_4$ FGD containing supplemental Mg) (Table 6). Plants grown with BP-#26 (FBC) accumulated potentially toxic concentrations of B at low levels of added compound to soil, but plants did not grow well in the experiment at levels $> 0.5\%$ and adequate DM was not obtained for analysis (Table 4). For those plants grown in acidic soil amended with the CCPs and having relatively high shoot B accumulation (Tables 4–6), B was also high in the original CCP (Table 1).

Attempts were made to add CCP levels to soil that would reduce plant DM below a maximum at some lower level. For the most part, this was accomplished by the CCPs added to this acidic soil. Nevertheless, plants grown in soil amended with three of the CCPs [BP-#18 (FA), BP-#16 and BP-#22 (high $CaSO_4$ FGDs)] had only slight DM reductions below a maximum. Plant reductions in DM from a maximum could potentially have been associated with high B accumulation in shoots of plants grown in acidic soil amended with six CCPs [BP-#12 and BP-#18 (FAs), BP-#5 and BP-#8 (stabilized high $CaSO_3$ FGDs), BP-#27 (high $CaSO_4$ FGD plus Mg), and possibly BP-#26 (FBC)]. Plants grown with soil amended with BP-#12 (Class C FA) and BP-#27 a (high $CaSO_4$ FGD with supplemental Mg) accumulated ~ 500 and ~ 300 mg kg^{-1} B, respectively, before DM decreased below a maximum (Tables 4 and 6).

In summary, some of the CCPs used in these studies increased accumulation of B in shoots to the extent that the B level could have been toxic. However, B toxicity did not appear to have been the only cause for plant reductions in DM when plants were grown in the acidic soil amended with CCPs. This maize hybrid may have been able to tolerate high shoot B concentrations. High soil pH and salt toxicity (high EC) could also have contributed to reduced DM for plants grown in this acidic soil amended with some of the CCPs. Production of toxic sulfur dioxide gas from high $CaSO_3$ FGD added to acidic soil [21] and imbalances of minerals like Ca and Mg (Mg deficiency) [22] can reduce plant growth when acidic soil has been amended with CCPs. Most of the CCPs used in these studies enhanced plant growth when added to this acidic soil at levels that would not increase B to toxic concentrations in plants and increase soil pH to abnormal values. Continual loading of CCPs could potentially induce B toxicity problems for plants over time. Either excess B should be leached from CCPs before adding to soil, or planting should be delayed after adding CCPs to soil to allow time for leaching by precipitation.

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